

Photovoltaic studies of (PbCrO₄–ZnO) thick binder layers

Meenu Singh and S G Prakash

Department of Electronics and Communication, University of Allahabad,
Allahabad-211 002, India

Received 20 March 1996, accepted 22 July 1996

Abstract : In this paper (PbCrO₄–ZnO) photovoltaic detectors have been reported, which were fabricated by embedding the sensitive material in polystyrene and sandwiching between the conducting surfaces of two plates. The optimum photovoltage has been observed for (25% PbCrO₄–75% ZnO) binder layer. The variations of photocurrent and photovoltage with time and intensity of illumination are investigated. An increase in open circuit output photovoltage and short circuit photocurrent was observed by connecting cells in series and parallel, respectively. The existence of discrete trap depths appears plausible for different compositions. *I–V* characteristics of photovoltaic cells have been observed for white light. The spectral response of (25% PbCrO₄–75% ZnO) cell has been observed and relative quantum efficiencies have been plotted.

Keywords : Photovoltaic cells, thick binder layer, polycrystalline material

PACS No. : 72.40.+w

The photovoltaic cell generates a voltage and/or current depending upon the illumination and the load [1]. There are a large variety of materials and material combinations, which have been investigated for their qualification for homojunction and heterojunction solar cells. The materials are binary and ternary III–V, II–VI and I–III–VI₂ compounds or even quaternary and pentenary compounds. A lot of photovoltaic studies have been made with thin films [2,3] and thin film diodes [2,4,5]. The commonly known photovoltaic cells are the cuprous oxide (Cu₂O) barrier cell and the selenium barrier layer cell. In this paper, an attempt has been made to study the photovoltaic effect in (PbCrO₄–ZnO) thick binder layers.

The main advantage of thin films and thick binder layers is their promise of low cost, due to low cost processing, and the use of relatively low cost materials. The industrial and military needs have encouraged the studies on such type of photovoltaic cells. Further, the

fabrication of thick binder layers is much easier than the thin films. However the speed of thick layers is comparatively slow due to presence of large density of trap levels. The disadvantage of thin films and thick layers are low efficiency and long-term instability. The low efficiency is caused by the grain boundary.

Besides *p-n* junction photovoltaic detectors, the photovoltaic effects are also observed in metal-semiconductor rectifying contacts (Schottky barriers). The photovoltaic cells with such type of contact have a transparent metal electrode at the front wall and a metal backing. In our experiment, the transparent metal electrode is a glass plate with a transparent conducting coating of tin oxide (SnO_2 , with band gap = 3.5 eV and electron affinity $\chi = 4.8$ eV). There are three photocurrent components flowing in the photovoltaic cell. Light with energy $h\nu > q\phi_B$ (the barrier height) can be absorbed in the metal and excite carriers (electrons or holes, depending upon the type of semiconductor) over the barrier into the semiconductor. Short-wavelength light entering the semiconductor is mainly absorbed in the depletion region. Long wavelength light is absorbed in the neutral region, creating electron-hole pairs just as in a *p-n* junction.

The I - V characteristics of a Schottky barrier under illumination is given by

$$I = I_S (e^{qV/kT} - 1) + I_{SC} \quad (1)$$

$$I = f(V) - I_{SC} \quad (2)$$

$$I_S = AA^{**}T^2 \exp(-q\phi_B/kT), \quad (3)$$

where

n = ideality factor,

A = Area of metal-semiconductor contact,

A^{**} = Effective Richardson constant,

$q\phi_B$ = barrier height,

I_{SC} = Short circuit current flowing in the cell, under illumination.

The open circuit photovoltaic voltage V_{OC} would follow from the equation

$$I = 0, \quad \text{or} \quad f(V_{OC}) = I_{SC}. \quad (4)$$

Samples were prepared by heat treatment technique. For this, high purity base materials i.e. PbCrO_4 and ZnO of different energy gaps 2.3 eV and 3.2 eV respectively were mixed in different proportion by weight and ground for homogeneous mixing. The mixtures were fired at 400°C in a cylindrical furnace in air atmosphere for 40 min.

The photovoltaic cells were fabricated in the sandwich type of parallel plate capacitors, for this the sensitive material was embedded in polystyrene binder and sandwiched between the conducting surfaces of two glass plates. One of the surfaces of glass plate was made conducting by spreading a layer of SnO_2 over it. The cells were deposited on an area varying $\sim 1.0 \text{ cm}^2$ to 6.0 cm^2 with thickness varying from 0.034 cm to 0.05 cm. The cell was kept in a dark metallic chamber with a slit on its top surface. Upper

surface of the cell could be illuminated with the help of a 300 W Hg-lamp. The measurements are usually done with solar lamp at 1.5 AM and 100 mW/cm^2 intensity. Intensity of illumination was varied by varying the sample to lamp distance and was measured using a luxmeter. The current and voltage were measured with the help of a nanoammeter and multimeter respectively. The various excitation wavelengths were selected by using optical filters.

Five samples having different compositions *i.e.* 100% PbCrO_4 , (75% $\text{PbCrO}_4\text{--}25\%$ ZnO), (50% $\text{PbCrO}_4\text{--}50\%$ ZnO), (25% $\text{PbCrO}_4\text{--}75\%$ ZnO) and 100% ZnO were prepared by heat treatment technique. The 100% ZnO and (50% $\text{PbCrO}_4\text{--}50\%$ ZnO) samples did not show photovoltaic effect. The maximum photovoltage and photocurrent was observed for (25% $\text{PbCrO}_4\text{--}75\%$ ZnO) samples fired at 400°C for 40 min. The effect of various parameters *i.e.* time, intensity of illumination, external load and combinations on photovoltage and photocurrent have been observed.

Rise and decay curves :

Rise and decay of short circuit photocurrent (I_{SC}) for different samples under white light intensity of 65 lux and 4300 lux are shown in Figure 1. No photovoltaic effect is shown by

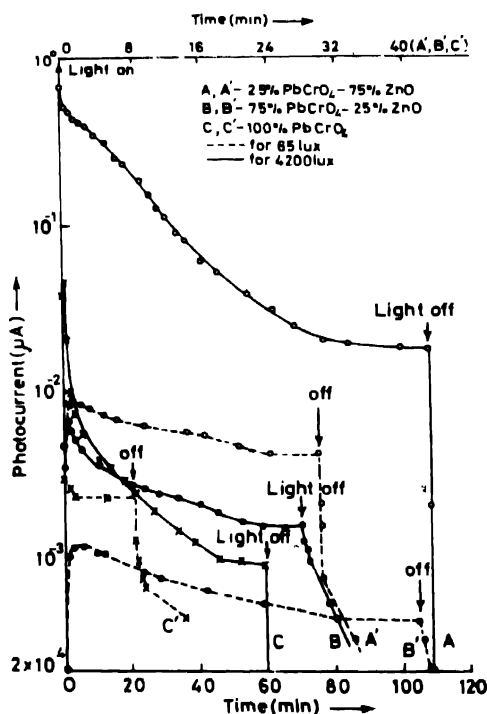


Figure 1. Rise and decay of photocurrent for different photovoltaic cells at different intensity of illumination. Solid line curves for white light intensity 4200 lux and dotted line curves for 65 lux, A, A' for 25% $\text{PbCrO}_4\text{--}75\%$ ZnO , B, B' for 75% $\text{PbCrO}_4\text{--}25\%$ ZnO and C, C' for 100% PbCrO_4 cells (Room temperature = 16°C)

100% ZnO and (50% PbCrO₄–50% ZnO) samples. The maximum short circuit photocurrent is obtained for (25% PbCrO₄–75% ZnO) sample. The photocurrent becomes zero for the 100% PbCrO₄ and (25% PbCrO₄–75% ZnO) samples when light is switched off. For all compositions the photocurrent rises as soon as the light is switched on but after acquiring a maximum value, it continues to decay for a very long time before obtaining a stable value *i.e.* both positive and negative photoconductivity [6] results, where negative photoconductivity is defined as the decrease in conductivity in presence of light. Positive photoconductivity in presence of light is due to the increase in density of electrons or holes or both. If with the elapse of time, the minority carriers are also excited from the imperfection centres, a negative photoconductivity results. This is due to the rapid recombination of minority carriers with majority carriers. This explains why negative photoconductivity occurs after positive photoconductivity.

The decay curves of photocurrent (*I*_{SC}) have been used to calculate the trap depths. The plots of log *I*_{SC} versus time for decay mode (Figure 1) show that decay can be governed by more than one exponential law. This is in accordance with Bube model [7]. This implies that the traps of different nature are situated at different energy depths below the lower edge of the conduction band.

The theory of Randall and Wilkins [8] for emptying of traps during decay assumes that the probability of an electron escaping from a trap is given by the equation

$$p = S \exp (- E / kT), \tag{5}$$

where *E* is trap depth, *k* is Boltzman constant, *T* is a absolute temperature and *S* is frequency factor of the order 10⁹.

The *p*-values corresponding to different exponential have been calculated by the relation

$$I_{SC} = I_{OSC} \exp (- pt), \tag{6}$$

where *I*_{OSC} is current at the moment when light is interrupted and *I*_{SC} is current at any instant of time (*t*).

The calculated *p*-values (slopes of the straight lines) for different samples are listed in Table 1.

Table 1. Calculated *p*-values for different samples

Composition		<i>p</i> × 10 ³					
		First		Second		Third	
		<i>exponential</i>		<i>exponential</i>		<i>exponential</i>	
		65 lux	4200 lux	65 lux	4200 lux	65 lux	4200 lux
100%	PbCrO ₄	17.7	6.96	–	2.34	–	–
75%	PbCrO ₄ –25% ZnO	121.2	270.3	8.12	–	1.42	–
25%	PbCrO ₄ –75% ZnO	138.5	73.3	3.4	–	–	–

The values of trap depths (E) corresponding to different exponential are calculated using (5) and (6) and is given by

$$E = kT \left[\log_e S - \log_e \frac{(\log_e I_{OSC} / I_{SC})}{t} \right] \quad (7)$$

The values of trap depths for different samples are listed in Table 2.

Table 2. Trap ionisation energies of different traps for different samples.

Composition	E (eV)					
	First		Second		Third	
	<i>exponential</i>		<i>exponential</i>		<i>exponential</i>	
	65 lux	4200 lux	65 lux	4200 lux	65 lux	4200 lux
100% PbCrO ₄	0.62	0.64	—	0.67	—	—
75% PbCrO ₄ -25% ZnO	0.57	0.55	0.64	—	0.68	—
25% PbCrO ₄ -75% ZnO	0.56	0.58	0.66	—	—	—

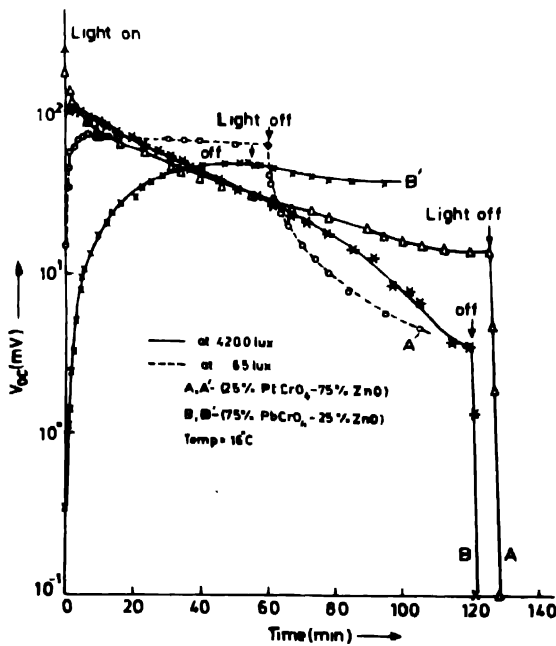


Figure 2. Rise and decay of open circuit photovoltage (V_{OC}) for different photovoltaic cells at different light intensities. Solid line curves for white light intensity 4200 lux and dotted line curves for 65 lux, A, A' for 25% PbCrO₄-75% ZnO, B, B' for 75% PbCrO₄-25% ZnO cells (Room temperature = 16°C).

Rise and decay of open circuit photovoltage for these compositions are shown in Figure 2. Photovoltage continues to increase tending towards a saturation value at lower intensity of illumination. When light is switched off, photovoltage decreases slowly to

reach the dark level. When the observations are taken at high intensity *i.e.* 4200 lux, photovoltage increases as soon as the light is switched on and after acquiring a maximum value, it continues to decay in presence of light. Slow rise and decay of photovoltage is due to the presence of deep traps as described earlier. The decrease in photovoltage in presence of light is due to the same reason which causes negative photoconductivity.

Effect of intensity of illumination :

Figure 3 shows the variation of short circuit photocurrent (I_{SC}) with intensity of illumination (I) for different samples on log-log scale. The curves are straight lines having different

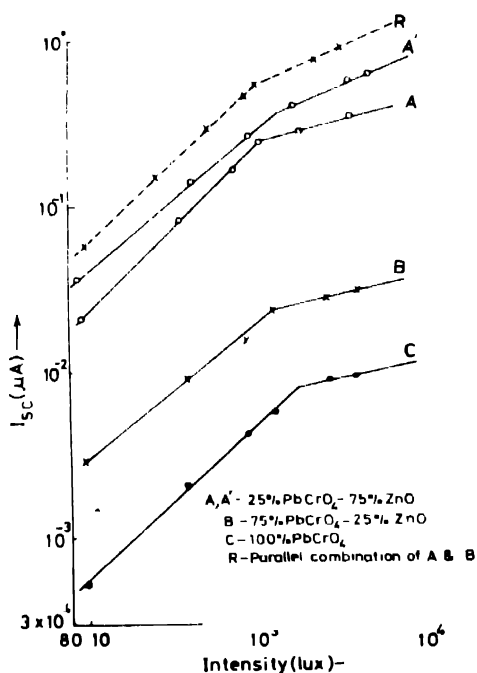


Figure 3. Variation of short circuit photocurrent (I_{SC}) with intensity of illumination for different photovoltaic cells and also parallel combination of two cells. Curve A, A' for two different 25% PbCrO_4 -75% ZnO cells, B for 75% PbCrO_4 -25% ZnO cell, C for 100% PbCrO_4 cell and curve R for parallel combination of two cells of 25% PbCrO_4 -75% ZnO of different area (3.6 cm^2 and 6 cm^2) (Room temperature = 16°C).

slopes for lower and higher light intensities. Thus the variation can be represented by relation $I_{SC} \propto I^\gamma$, where γ is the slope of any straight line section. For all compositions, short circuit photocurrent varies sublinearly ($\gamma < 1$) with light intensity. This suggests, a continuous trap distribution but rather exponential in nature, below the edge of the conduction band. An increase in intensity would convert more of the trap levels to recombination levels, thereby decreasing the electron life time and giving rise to observe sublinearity [9].

The output current may be increased by connecting several photovoltaic cell in parallel. This effect is shown in Figure 3. This figure shows the variations of I_{SC} with light intensity for two (25% PbCrO₄-75% ZnO) cells of different areas (curves A and A') and their parallel combination (curve R).

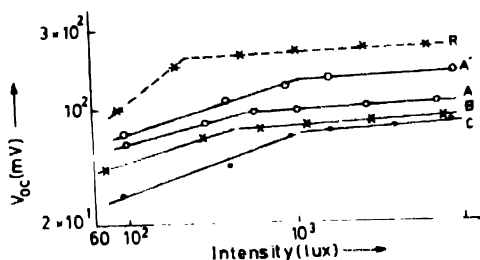


Figure 4. Variation of open circuit photovoltage (V_{OC}) with intensity of illumination for different photovoltaic cells : Curve A, A' for two different 25% PbCrO₄-75% ZnO cells, B for 75% PbCrO₄-25% ZnO cell, C for 100% PbCrO₄ cell and curve R for series combination of two cells of 25% PbCrO₄-75% ZnO of different area (3.6 cm² and 6 cm²) (Room temperature = 16°C)

Figure 4 shows the variation of open circuit photovoltage (V_{OC}) with intensity of illumination (L) for different compositions. This figure also shows the variation of the V_{OC} with light intensity for series combination (R) of two different (25% PbCrO₄-75% ZnO) photovoltaic cells of different areas (curves A and A'). This shows that resultant open circuit photovoltage can be increased by connecting two cells in series. For all compositions V_{OC} varies sublinearly ($\gamma < 1$) with intensity of illumination.

I-V characteristics :

Figure 5 shows the current-voltage characteristics of photovoltaic cells for white light (1200 lux) curves normalised w.r.t. 100 mW/cm². The measurements could not be taken with standard solar lamp at 1.5 AM due to limitations. The intersections with axes yield the short circuit current (I_{SC}) and open circuit voltage (V_{OC}). The region of maximum output power

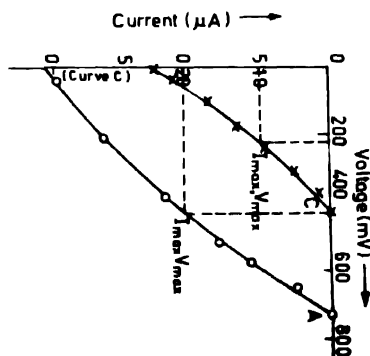


Figure 5. *I-V* Characteristics for different cells : A for 25% PbCrO₄-75% ZnO cell C for 100% PbCrO₄ cell (white light intensity = 1200 lux, cell area = 1 cm², room temperature = 28°C).

of the cell is indicated in Figure 5 by the dotted line area. At the maximum power point V and I have been used to calculate maximum output power $(IV)_{\max}$, fill factor (FF) and efficiency (η) of the cell.

The fill factor is defined as

$$F.F = \frac{\text{Maximum output power}}{I_{SC} \cdot V_{OC}} = \frac{(IV)_{\max}}{I_{SC} \cdot V_{OC}} \quad (8)$$

The cell efficiency is given by

$$\eta = \frac{\text{Maximum output power (Watts)}}{\text{Area of cell (m}^2\text{)} \times \text{Incident irradiance (watts / m}^2\text{)}} \times 100\% \quad (9)$$

The series (R_s) and shunt resistance (R_{sh}) are calculated by slopes using expressions [10]

$$R_s = - \left(\frac{\partial V}{\partial I} \right) I = I_{SC} \quad (10)$$

$$R_{sh} = - \left(\frac{\partial V}{\partial I} \right) V = V_{OC} \quad (11)$$

Using eqs. [(8)–(11)] the FF , η , R_s and R_{sh} have been calculated and listed in Table 3.

Table 3. Calculated values of FF , η , R_s and R_{sh} for different samples.

Composition	Efficiency (η)	FF	R_s ($k\Omega$)	R_{sh} ($K\Omega$)
100% $PbCrO_4$	0.005	0.21	242.8	119.0
25% $PbCrO_4$ –75% ZnO	0.04	0.31	25.6	15.6

Spectral response :

Figure 6 shows the normalized spectral response for standard N/P Si solar cell (curve B) [11] and (25% $PbCrO_4$ –75% ZnO) photovoltaic cell (curve A).

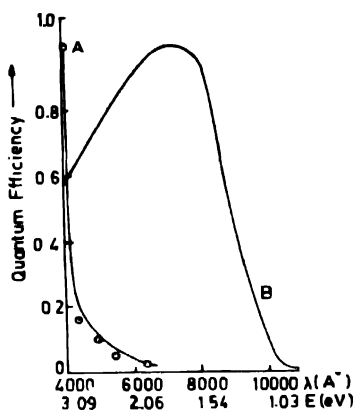


Figure 6. Quantum efficiency curves, A for (25% $PbCrO_4$ –75% ZnO) cell and B for standard n/p Si solar cell

The photocurrent collected at each wavelength relative to the number of photons incident on the surface at that wavelength determines the spectral response of the device also known as quantum efficiency [2,1]. The quantum efficiency is given by relation

$$\eta_q = \left(\frac{I_p}{q} \right) / \frac{P_{opt}}{h\nu}, \quad (12)$$

where I_p is photogenerated current, P_{opt} is incident optical power and $h\nu$ is photon energy. The maximum I_{ph} has been normalized to unity. The curve mostly lies in UV region, and does not show a maxima, whereas the spectral response of standard Si cell is spread in visible region having a maxima at $\approx 7000 \text{ \AA}$. The difference in nature is perhaps due to larger energy gap of (PbCrO₄-ZnO) system.

Maximum short circuit current and open circuit voltage are obtained for (25% PbCrO₄-75% ZnO) sample. The 100% ZnO and (50% PbCrO₄-50% ZnO) samples do not show photovoltaic effect. The output voltage and current can be increased by connecting cells in series and parallel respectively. The existence of discrete trap depths appears plausible for different compositions. The value of V_{OC} and I_{SC} is rather small because the resistance of the cell due to thick binder layer is quite large ($\approx M\Omega$). The efficiency of the 100% PbCrO₄ cell can be improved by mixing ZnO. The spectral response characteristic of (25% PbCrO₄-75% ZnO) cell shows that optimum value of I_{SC} is observed for lower wavelength i.e. for higher energy of radiation. Such a cell is effective in UV region.

References

- [1] R W Smith and A Rose *Phys. Rev.* **97** 1531 (1955)
- [2] S M Sze *Physics of Semiconductor Devices* (New Delhi : Wiley Eastern) (1981)
- [3] A Ahlstrom and W W Gartner *Appl. Phys.* **33** 2602 (1962)
- [4] Om Prakash, C Sindhu R and M Gangey *IETE Tech. Rev.* **10** 579 (1993)
- [5] P Nubile *Solid State Electron.* **32** 945 (1995)
- [6] R H Bube *Photoconductivity of Solids* (New York : John Wiley) (1967)
- [7] R H Bube *Phys. Rev.* **80** 655 (1950)
- [8] J T Randall and M H F Wilkins *Proc. Roy. Soc.* **A184** 366, 390 (1945)
- [9] P K C Pillai, N Schroff, N Nand Kumar and A K Tripathi *Phys. Rev.* **32** 8228 (1985)
- [10] A Polman, W G J H M Van Sark, W Sinke and F W Saris *Solar Cells* **17** 241 (1986)
- [11] Harold J Hovel *Semiconductors and Semimetals* (New York : Academic) (1975)